INSTRUMENTATION FOR STUDY OF NANOMATERIALS IN NPI REZ

(New laboratory for material study in Nuclear Physics Institute in Rez)

Václav BEJŠOVEC, Antonino CÁNNAVO, Giovanni CECCIO, Vladimír HNATOWICZ, Pavel HORÁK, Vasily LAVRENTIEV, Anna MACKOVÁ, Ivo TOMANDL, Alfio TORRISI, Jiří VACÍK

Nuclear Physics Institute (NPI) of Academy of Sciences of the Czech Republic, Rez, phorak@ujf.cas.cz

Abstract

Nano-sized materials become irreplaceable component of a number of devices for every aspect of human life. The development of new materials and deepening of the current knowledge require a set of specialized techniques - deposition methods for preparation/modification of the materials and analytical tools for proper understanding of their properties. A thoroughly equipped research centers become the requirement for the advance and development not only in nano-sized field.

The Center of Accelerators and Nuclear Analytical Methods (CANAM) in the Nuclear Physics Institute (NPI) comprises a unique set of techniques for the synthesis or modification of nanostructured materials and systems, and their characterization using ion beam, neutron beam and microscopy imaging techniques. The methods are used for investigation of a broad range of nano-sized materials and structures based on metal oxides, nitrides, carbides, carbon-based materials (polymers, fullerenes, graphenes, etc.) and nano-laminate composites (MAX phases).

These materials can be prepared at NPI using ion beam sputtering, physical vapor deposition and molecular beam epitaxy. Based on the deposition method and parameters, the samples can be tuned to possess specific properties, e.g., composition, thickness (nm - μm), surface roughness, optical and electrical properties, etc.

Various nuclear analytical methods are applied for the sample characterization. RBS, RBS-channeling, PIXE, PIGE, micro-beam analyses and Transmission Spectroscopy are accomplished at the Tandetron 4130MC accelerator, and additionally the Neutron Depth Profiling (NDP) and Prompt Gamma Neutron Activation (PGNA) analyses are performed at an external neutron beam from the LVR-15 research reactor.

The multimode AFM facility provides further surface related information, magnetic/electrical properties with nano-metric precision, nano-indentation, etc.

Keywords: LEIF, MBE, AFM, PVD, Ion Beam Analysis, Ion scattering, NDP, Microbeam

1. INTRODUCTION

Nanostructured materials with a characteristic length scale of which is below 100 nm, have specific properties deviating from those of bulk ones. This deviation results from the reduced size and/or dimensionality, as well as from the numerous interfaces between adjacent crystallites or layers. The synthesis of materials and/or structures with new properties is an emerging interdisciplinary field based on solid state physics, chemistry and materials science [1]. The research in the new laboratory is mostly focused on preparation and characterization of two-dimensional thin films and nano-laminate structures (MAX phases) exhibiting nanoscale features. The structures are based on combinations of inorganic materials, metals, synthetic polymers and carbon allotropes. Here, only the MAX phases are mentioned in details. These composites have a layered structure of the hexagonal carbides and nitrides that were discovered in the 1960s. They exhibit unusual chemical, physical, electrical, and mechanical properties under various conditions [2]. The MAX phases are bridging the gap between metals and ceramics. For this reason they have become an object of intensive research. They exhibit a high potential applicability in different technologies, such as high efficiency

engines, or damage-tolerant systems. Despite of the rather long lasting research, there remain open scientific questions to answer, as well as technological hurdles to overcome. In our laboratory the first MAX phase specimens have been already prepared and characterized by various methods. The techniques of the laboratory are briefly described in the following paragraph.

2. INSTRUMENTATION AVAILABLE AT THE NPI

2.1. Low energy ion facility (LEIF)

The Low Energy Ion Facility (LEIF) established recently in the NPI is a modular system developed for the fundamental research in the field of materials science. The system (**Figure 1**) is divided into two lines with the first line consisting of ion source, ion optics chamber, ion beam diagnostics and a sputtering chamber. After the sputtering chamber, a 1T separation magnet bends the ion beam to 90° and directs it through ion diagnostics unit and quadrupole magnetic optics into the implantation/analytical chamber.

The fundamental element of the system is the multicusp ion source capable of producing uniform, high density plasma with a high gas and electrical efficiency. A filament (based on the thoriated tungsten wire) is surrounded by eight permanent magnets to produce a beam of single and multiple charged ions with the current of tens of nA up to hundreds of μA. In the anode area a small vessel is placed in order to generate ion species not only from gases but also from solid compounds. The maximum voltage applied on the ion source is 35 kV, thus generating the ion beam with the energy up to 35 keV for single charged ions.

The ion beam extracted from the source by the movable extraction electrode is shaped by the Einzel lense system and directed to the sputtering chamber, where the Ion Beam Sputtering (IBS) is utilized for the production of thin layers with thicknesses up to hundreds of nm. In another regime, the beam can be directed through the first chamber to the bending separation magnet, where only ions with specific A/Z ration are selected. The ions are used for irradiation, implantation of samples within the implantation/analytical chamber. The magnet is designed to separate ion species with the energy of 35 keV and A/Z ratios up to 200, so that the implantation within a broad spectrum of ions to the ion fluencies from 1e14 - 1e17 ions/cm^2 is possible.

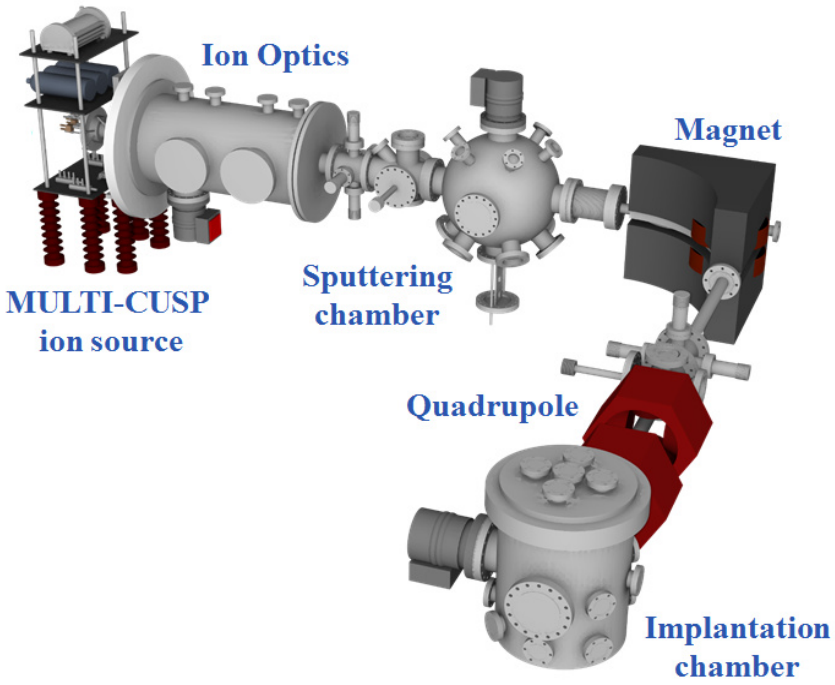

Figure 1 The schematics of the Low Energy Ion Facility (LEIF)

2.2. MBE

Molecular beam epitaxy (MBE) is an Ultra-High-Vacuum (UHV) device for production of epitaxial structures with high purity, uniformity and monolayer control.

The physical working-principle of MBE is based on the interaction between molecular or atomic beams (provided by evaporation in the effusion cells) and a heated crystalline substrate. Despite the conceptual simplicity, this technique needs particular technological requirements to be fulfilled. The Ultra-High-Vacuum operation, i.e., p = 10^{-9} Pa, is a mandatory condition because it guarantees the highest purity of growing material, permitting the use of electron diffraction probes as diagnostic tool. The abruptness, variable growth temperature (20 - 500 °C) and the low growth rate (1 μm/h) makes possible to control of interfaces and doping profiles.

The MBE system installed in NPI is equipped with 2 electron guns and a Knudsen cell as a molecular beam sources. Pyrolytic boron nitride (PBN) is chosen for the crucibles which gives a low rate of gas evolution and chemical stability up to 1400 °C. Careful variation of the temperatures of the cells via PID controllers permits the control of the intensity of the flux of every component or dopant of better than 1 %. An additional ion gun is present for Ion Beam Assisted Deposition (IBAD). A special UHV positioning system allows rotation and 3D manipulation of the substrate to improve the growth homogeneity. Tantalum shutters permit the control of composition and doping of the growing structure.

The in-situ characterization tool is the RHEED (reflection high energy electron diffraction) system. The oscillation of the RHEED signal exactly corresponds to the time needed to grow a monolayer and the diffraction pattern on the RHEED window gives direct indication over the state of the surface. The main deposition chamber can be connected to an additional analytical chamber for ex-situ sample analyses by, e.g., atomic force microscopy, van der Pauw method and low energy electron diffraction.

2.3. PVD-C-plus facility

Fabrication of metal-organic hybrid nanomaterials is presently one of the crucial topics of modern nanoscience promising new fundamental fields and advanced applications. We contribute to this topic using our PVD system (physical vapor deposition, PVD) designed for the controlled fabrication of the Me-C60 hetero-nanostructures (we call this system as “PVD-C-plus” facility). The PVD system can also be applied for fabrication of pure C60 or other C-nanostructures, as well as for fabrication of pure metals and silicon. Variety of hybrid nanostructures combining the components from the former (i.e., C-materials) and the latter (metals and Si) groups can be also produced under this PVD facility.

Operation of the PVD system implies a proper adjustment of setup parameters, which allow to design rather complex nanostructures. Deposition of thin films (up to 200 nm in thickness) of the materials occurs in a high vacuum (up to 10^{-6} mbar) on nonvolatile solid substrates kept at the temperature ranging from RT to 500 ºC. Deposition of thin films can be realized through thermal evaporation of the materials using two kinds of sources, namely mini-effusion cell (MEC) and electron gun (EG). The MEC source is used for evaporation of C60, as well as the EG can be used for evaporation of metals and Si. Parameters of deposition influencing the film composition, nanostructure and thickness can be tuned precisely with the digital controllers driving the efficiency of the deposition process with high precision. Design of the hybrid nanostructures also implies the proper use of electrical shutters and digital quartz thickness monitor, which are equipped inside of the vacuum chamber of the PVD system.

2.4. NTEGRA Aura AFM system

The main instrument able to perform a comprehensive test of our deposited films or other suitable samples is the commercial atomic force microscope (AFM) called as NTEGRA Aura (producer is NT-MDT). The NTEGRA Aura is an advanced, powerful and complex AFM system possessing a modular design and including all

functional opportunities of the AFM method known at present. The modular structure allows one to upgrade the system continuously and to realize a specific design of each experiment that greatly improve a research potential of this system.

The main feature of the NTEGRA Aura is a possibility to realize the AFM experiment in vacuum or in controllable gas atmosphere (N_2, O_2, Ar, etc.). Our AFM system also includes other important opportunities, such as heating of the sample (up to 120 ºC) and application of the external magnetic fields with in-plane and out-of-plane orientations of the magnetic vectors. Depending on the sample origin and the required task, we can apply contact, semi-contact (tapping) and non-contact scanning modes, which can yield a unique 3D pictures of the surface nanostructure (with resolution of 1 nm), unique information about the local mechanical (elasticity, friction), electrical or magnetic properties of the sample surface (with resolution of 10 nm). The research importance of the AFM system are related also with the opportunity to perform spectroscopic analysis in a certain point of the sample surface in order to clarify origin of some selected nano-object. The scientific opportunities of our AFM system is greatly enhanced in scanning tunneling microscopy (STM) mode, which allows to study the surface under atomic resolution. The latter mode, however, requires the samples with special (atomically-flat and clean) surfaces and with rather good conductivity. The digital PX-controller provides a high functionally of all AFM modes with negligible electrical noise.

2.5. ITS

Ion Transmission Spectroscopy (ITS) [3] is a specific method of non-destructive examination of inhomogenities in thin films (e.g., presence of micro-channels or pores). ITS is based on measuring of energy loss of the mono-energetic charged particles passing through the film. The mono-energetic beam of alpha particles from radioactive ^{241}Am source or from Tandetron 4130MC accelerator are used. The transmitted particles are detected by the Si detector connected to a standard spectrometric chain. The energy spectra are evaluated off-line by a computer code (developed at the NPI Rez for laboratory purposes). The energy spectra of particles reflect not only the presence of inhomogenities, but also their size and form.

2.6. NDP/PGAA

The Neutron Depth Profiling (NDP) [4] is a nondestructive nuclear analytical technique based on measurement of energies of reaction products from nuclear reactions of certain light isotopes with thermal neutrons (E_n = 0.025 eV). The emission of reaction products is isotropic and the detector can be placed at any angle with respect to the sample surface. In the Nuclear Physics Institute at Rez, a 5.6 m long neutron guide was installed at the LVR-15 nuclear research reactor (the reactor is operated by Research Center Rez). The neutron guide provides a thermal neutron beam of 10^7 n·cm^2·s^{-1} intensity and Cadmium Ratio (R_{Cd}) = 10^5 with a beam dimension of 4 mm (height) x 80 mm (width). A classical reaction that can be studied by NDP is ^{6}Li(n,α)^{3}H. In this reaction, thermal neutrons induce an intensive, isotropic nuclear reaction (n, α) on the ^{6}Li isotope producing two reaction products, α (2.055 MeV) and ^{3}H (2.727 MeV), that are emitted from the sample in opposite directions. Even though the natural abundance of the ^{6}Li isotope is only about 7.5 %, the high cross section (940 barns) assures (under the intense neutron beam bombardment) a fast data collection. This reaction is investigated for important application, such as thin Li ion batteries, important and actual research topic.

2.7. RBS, NRA, ERDA and RBS/Channeling

The Rutherford Back-Scattering (RBS) [5] is a non-destructive analytical method based on elastic scattering of impacting particles. Protons, alpha particles or heavier ions (produced by the Tandetron MC 4130 accelerator) with energy from few keV to tens of MeV are penetrating a sample where these species are scattered and subsequently detected by the detection system. In NPI the solid state detector with energy resolution of 15 keV is placed at the angle of 170°. From the obtained energetic spectrum of scattered particles and intensity of individual components it is possible to identify presence of specific elements, as well as its concentration and spatial distribution.

The RBS technique in its most common setup, i.e., alpha particles with energy of 2000 keV, is more suitable for the detection of heavier elements within the sample composed of lighter elements. In this situation it is possible to detect elements on an areal concentration level of 10^{12} - 10^{13} at/cm^2. The accessible depth resolution is ca 10 nm. To analyze the concentration of lighter elements, a modification of the method is necessary. For elements, such as C or O, an ion beam of specific energy can be used so the impacting particles penetrate the atomic core, resonance occurs and the significantly increased cross-section allows the estimation of these elements even within heavier matrix. This analysis is called Nuclear Reaction Analysis, NRA. Other possibility is a method of Elastic Recoil Detection Analysis, ERDA, where instead of scattered particles the particle recoiled from the samples are detected.

A special variant of the RBS technique is RBS/Channeling [5]. In this mode the collimated beam of particles irradiates the sample in the direction of one of the crystal planes. Most of the impacting particles are in this situation funneled into channels formed by the organized rows of atoms. Channeling particles do not get into the contact with atomic cores and thus the probability of scattering is much lower. Presence of other elements, interstitials or defects will be observed as significant increase of the intensity of recoiled particles. RBS/Channeling is thus an importing method providing unique information about the crystal structure.

2.8. PIXE/PIGE

In contrast with the RBS technique, the Proton Induced X-ray/Γ-ray emission methods are based on inelastic interaction between incident proton and the sample material (experimental set-up is depicted in the **Figure 2a**). In case of PIXE, the characteristic X-ray radiation occurs as a result of the interaction between incident proton and electrons in atomic shell. The particle can eject electron from the inner shell of the atoms that is replaced by the electron from the outer shell. The energy difference between these two levels is ejected in the form of X-ray radiation. Under feasible conditions, i.e., heavier elements within the light matrix, the detection limit of the PIXE method can be below 1 ppm. The PIXE method is an important technique for analysis of trace elements within the biological samples (Pb, As, Hg, Cd, etc.). It is also a valuable tool in the analysis of the composition of aerosols in the air created as a result of burning of fossil fuels (analysis of traces of toxic elements).

The Proton Induced Γ-ray emission is a versatile, non-destructive analytical method based on the (p,γ) reaction. In this case, the incident proton causes excitation of the atomic core of the sample element. In a short time, the core returns to the basic level and the energetic difference is emitted as γ-ray. The energy and the number of photons is detected by the HPGe detector and from the spectrum elements in the sample can be identified. The concentration of the elements is measured with the help of the standard sample. For protons with energies from 1 to 3 MeV, the best sensitivities was found for Li, B, F, Na, and Al. The highest cross sections are for light isotopes (A<30), which can be determined with a sensitivity of 10 μg. g^{-1} or less.

2.9. Microbeam

One of the beam lines connected to the Tandetron MC 4130 accelerator in NPI (**Figure 2b**) is used for the analysis and modifications of a sample at small scale. The ion beam from the accelerator passes through a lens, i.e., a combination of magnetic quadrupoles with alternated polarities that focuses the beam to a spot as small as hundreds of nm in diameter. Standard IBA techniques (mainly PIXE, RBS, and NRA) are used to characterize the irradiated object. By raster-scanning the beam over the sample surface, 2D or 3D distribution of elements can be determined with nm depth resolution and lateral resolution limited by the size of the beam spot. The mapped area is from ca 10x10 μm up to 1x1 mm in size.

When samples cannot be measured in vacuum (due to their size, or presence of volatile components), a setup with an external ion beam can be used. Such arrangement is often applied for archaeological artefact or artworks. The ion beam is extracted from the chamber/beam line into air through a thin window. The sample is surrounded by an array of detectors (X-ray detectors for soft and hard X-rays etc.) obtaining the information

on the sample composition and concentration. The IBA methods can be employed on the external microbeam, either individually or in the PIXE-PIGE-RBS combination.

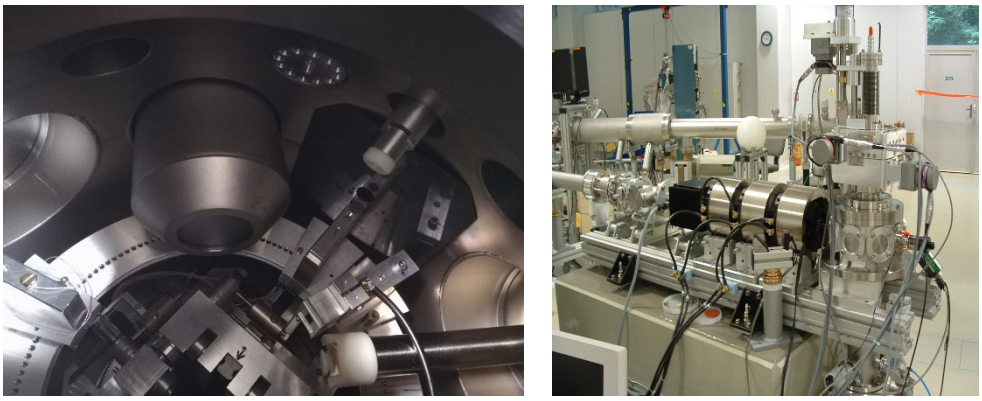

Figure 2 Instrumentation in NPI; 2a - Analytical chamber with multiple detectors for PIXE, PIGE and RBS measurement, 2b - The microbeam system

3. CONCLUSION

A laboratory complex has been developed at NPI SCR Rez, which is endowed with various standard deposition and analytical techniques for preparation and characterization of new prospective nano- and micro-structured systems. The uniqueness of the laboratory lies in combination of common techniques with diagnostic methods making use of charged particle and neutron beams. Most important are the devices for vacuum deposition, deposition by ion sputtering, ion implantation and by molecular beam epitaxy (MBE). Full spectrum of the IBA methods together with Neutron Depth Profiling (NDP) and Ion Transmission Spectroscopy (ITS) is used for specimen characterization. Complementary information on the structure, composition and properties of specimens are obtained with Atomic Force Microscopy (AFM) and using other techniques (FTIR, Raman, XRD, nano-indentation, SEM, TEM, HRTEM, etc.) available at collaborating organizations.

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REFERENCES

[1] H. Gleiter, Acta Materialia, Volume 48, Issue 1, 1 January 2000, Pages 1-29

[2] Barsoum, M.W. (2006) "Physical Properties of the MAX Phases" in Encyclopedia of Materials Science and Technology, K. H. J. Buschow (eds.). Elsevier, Amsterdam.

[3] J.Vacik, J.Cervena, V.Hnatowicz, D.Fink, Y.Kobayashi, K.Hirata, P.Y.Apel and P.Strauss, Study of latent and etched tracks by a charge particle transmission technique, Radiation Measurements 31 (1999) 81-84.

[4] D. Fink, Neutron depth profiling, *Hahn-Meitner-Institute, Report* HMI-B 539 (1996).

[5] Y. Wang, M. Nastasi, Handbook of Modern Ion-Beam Materials Analysis, Materials Research Society, Pittsburgh, 2009.